RHEOLOGICAL PROPERTIES OF ASPHALT CROSSBLENDS

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Key words: asphalt compatibility, size exclusion chromatography, rheology

ABSTRACT

Properties of blends of asphalts from different sources can not necessarily be predicted by averaging properties of the components. Asphalts may be considered to be combinations of a dispersed and a solvent moiety, the nature and amounts of which vary among asphalts. Asphalt properties will be determined by the manner in which the two moieties interact. In this work, dispersed and solvent moieties were generated from eight asphalts by size exclusion chromatography. Crossblended mixtures of dispersed and solvent moieties from different asphalts were prepared and their rheological properties measured. The influence of the relative amounts and nature of the two moieties on rheological properties were determined. It was found that rheological properties of the crossblended mixtures were greatly affected by the relative amounts of the two moieties. The nature of the two moieties also was influential in determining rheological properties, as the solvent components of some asphalts were found to be compatible with the dispersed moieties of some asphalts but incompatible with others.

INTRODUCTION

The compatibility of asphalt systems long has been of interest to researchers. Traxler[1] discusses the difference in properties among what are designated as compatible (sol-type) and non-compatible (gel-type) asphalts. According to Traxler, well-dispersed, compatible asphalts exhibit high temperature susceptibility of viscosity, high ductility, low elasticity, and low rates of oxidative age hardening. Non-compatible asphalts, which are poorly dispersed, are characterized by low temperature susceptibility, low ductility, pronounced elasticity, and high aging rates. These and other physical properties serve to categorize asphalts according to compatibility. The two fundamental types of asphalts will, of course, vary markedly in pavement performance.

Asphalt compatibility also is related to chemical composition. Non-compatible asphalts tend to be high in asphaltene and sulfur content compared with compatible systems. Heithaus[2] published a laboratory method that assigns numerical values to asphalts and asphalt blends according to compatibility. Heithaus considered asphalts to be dispersions of asphaltenes in a maltene solvent, and asphalt and asphalt blend properties therefore should be determined by the relative amounts of the two materials and the effectiveness by which maltenes disperse asphaltenes. The properties of asphalt blends thus are not necessarily computed additively from properties of their parent asphalts.

Properties of blends of various fractions of different asphalts have been studied. Altgelt and Harle[3] measured rheological properties of various asphaltene-maltene combinations. Traxler[4] studied mixtures prepared using solvent-derived fractions. During the Strategic Highway Research Program (SHRP)[5], mixtures of asphalt fractions prepared by size exclusion chromatography (SEC) were studied. Very large differences in rheological properties of crossblended mixtures of asphalt SEC fractions from different sources were observed. The SEC fractions were chosen because the separation method fractionates solutions of asphalts according to molecular size. If asphalts consist of a dispersed and a dispersing component, the dispersed component should consist of the more polar, aromatic constituents of asphalts, which should be of higher apparent molecular weight than the dispersing, or solvent, component.[6] The two components thus should be to some degree separable by SEC. A large number of asphalts have been separated into two SEC fractions that are believed to approximate asphalt dispersed and solvent components. The properties of the two components have been measured for these asphalts and vary according to source.[5] Relative amounts of the two fractions also vary considerably among asphalts, and this relative abundance of the two SEC fractions in an asphalt is termed the natural abundance ratio. The two fractions are designated SEC Fraction-I and SEC Fraction-II, which correspond to the dispersed and solvent components of asphalts respectively. The relative amounts of the two SEC fractions in an asphalt do not correspond to asphaltene and maltene yields.

Rheological properties of asphalts depend on relative amounts of dispersed and solvent components. The solvent component is much less viscous and less elastic than the dispersed component, which contains the viscosity-building constituents. Presumably, the nature of the two components and the manner of their interaction also affect rheological properties. Another physical property, the glass transition temperature, is determined by the relative amount of the two components and the source of the solvent component, but not the source of the dispersed component.[7] Other properties conceivably might depend more on the source of the dispersed component than the solvent. It is the goal of this study to quantify the influence of these three factors, source of solvent component, source of dispersed component, and relative amounts of the two, on asphalt rheological properties.

EXPERIMENTAL

The separation of asphalts into two fractions by SEC has been described previously.[8] The SEC Fraction-I materials are friable solids, and the SEC Fraction-II materials are viscous liquids. Crossblended mixtures were prepared by dissolving weighted fractions of each of two different SEC fractions in dichloromethane and combining the two solutions in a round-bottom flask. The flask was attached to a rotary evaporator and was immersed in a water bath. Most solvent was removed by heating the flask to 90°C (194°F) for one hour under vacuum. Residual solvent was removed by replacing the water bath with an oil bath and heating the flask to 130°C (266°F) under vacuum for one hour. The flask and contents were flooded with an inert gas and stoppered. Rheological measurements on the crossblended mixtures were obtained at 25°C (77°F) using a Rheometrics mechanical spectrometer. Usually, 8 mm plates were used, and strain rates of 3-15% were employed, depending on sample stiffness. Phase angles and dynamic shear modulus values were obtained over a wide range of shear rates to generate the Black plots in Figures 1-7. Each sample was annealed before rheological analysis.[8] If this step is not performed, erratic viscosity determinations are observed.

DISCUSSION

As stated above, the purpose of this work is to evaluate the compatibilities of crossblended mixtures of SEC fractions of asphalts and evaluate the influence of three factors on crossblend rheology. The three factors are the source of SEC Fraction-II (solvent), the source of SEC Fraction-I (dispersed component), and relative amount of each fraction in the crossblended mixture.

Eight asphalts studied in SHRP were separated into SEC Fractions I and II by SEC. These eight asphalts, called core asphalts, were intensively studied. They are coded as listed in Table 1, which also lists amounts of each of the two SEC fractions in each asphalt. These amounts are the natural abundance levels, and they vary considerably.

Seven sets of crossblended mixtures were prepared. Each set consists of eight members. In each set, the SEC Fraction-II component is the same. The SEC Fraction-I component is varied among members of the set. The ratio of components for each set is that of the parent asphalt of the SEC Fraction-II component. No set of crossblends was prepared from the SEC Fraction-II of asphalt AAM-1, because of the high natural abundance of SEC Fraction-I in this asphalt. Crossblends involving the SEC Fraction-II of AAM-1 have very high viscosities.[5]

Table 2 lists absolute viscosities of seven sets of crossblended mixtures at 25°C (77°F) and 1.0 rad/s. Each column in Table 2 corresponds to one of the seven sets of crossblends, in which the relative abundance of the two SEC fractions and the nature of the SEC Fraction-II are constant. In each column of data, only the source of the SEC Fraction-I changes from entry to entry down a column. Each row in Table 2 lists viscosities of crossblends in which the SEC Fraction-I source is constant. The SEC Fraction-II source and the relative abundance of the two fractions change from entry to entry along a row.

The entries in Table 2 in which both the SEC fractions are derived from the same source correspond to reconstituted parent asphalts. The viscosities of these mixtures are observed to be two to three times larger than the original asphalts. This is because light ends are lost in the workup process, resulting in somewhat enhanced viscosities in the reconstituted mixtures.

Figures 1-7 are Black plots of rheological data collected on the mechanical spectrometer for the seven sets of crossblends. Dynamic moduli (G^*) values at 25°C (77°F) were measured for each mixture at numerous rates of shear, and the value of the phase angle (δ) at each rate of shear was plotted against the G^* value. Low δ values indicate substantial elastic components in an asphalt, and vice versa. Asphalts whose Black plots exhibit large δ changes for a given range of G^* are shear susceptible. All crossblended mixtures whose Black plots are illustrated in Figure 1 contain 78.3 mass % of SEC Fraction-II of AAA-1. The Black plots of the eight different mixtures vary greatly. The mixture containing SEC Fraction-I of AAD-1 is very distinct from the other seven in that δ values in the Black plot are lower for a given G^* value and do not range over wide values of δ. This means that the mixture containing SEC Fraction-I of AAD-1 contains the largest elastic component and is least shear susceptible. On the right side of Figure 1, the mixture containing SEC Fraction-I of AAM-1 is characterized by much larger δ values and lower G^* values. The Black plot of this mixture indicates that its rheological properties will be very different from those of the mixture containing SEC Fraction-I of AAD-1. Due to the composition of the mixtures, the difference must be caused by the nature of the SEC Fraction-I materials. In Figure 1, the curve corresponding to the mixture containing SEC Fraction-I of AAG-1 also is somewhat distinctive. This curve ranges over a wide δ range, indicating that the mixture is highly shear susceptible. The curves corresponding to mixtures containing SEC Fraction-I of AAA-1, AAB-1, AAC-1, and AAF-1 are virtually superimposable. The curve corresponding to the mixture containing SEC Fraction-I of AAK-1 shows that this mixture is not as shear susceptible as most of the other mixtures.

The Black plots of the other six sets of mixtures exhibit similar trends to those observed in Figure 1 (Figures 2-7). Curves representing rheological data for mixtures containing SEC Fraction-I of AAD-1 lie at the lowest values of δ for a given range of G* values, and curves representing rheological data for mixtures containing SEC Fraction-I of AAM-1 exhibit contrary characteristics. In Figure 6, the differences are not very pronounced. This is because the concentration of SEC Fraction-I materials in asphalt AAG-1 is low. The mixtures containing SEC Fraction-I of AAG-1 are most shear susceptible, based on inspection of the Black plots. Again, the lines in Figure 6 are not sufficiently differentiated to demonstrate this tendency. Curves representing rheological data for mixtures containing SEC Fraction-I of the other five asphalts are more or less similar and are intermediate between the other three curves. In Figures 1, 2, 4, and 8, the Black plots of mixtures containing SEC Fraction-I of AAK-1 indicate that these mixtures are relatively less shear susceptible.

The Black plots of the mixtures, and correspondingly their rheological properties, become more distinct as the concentration of SEC Fraction-I in the mixture increases, and vice versa.

Reduced specific viscosities of all the crossblended mixtures have been calculated and are listed in Table 3. In order to do this, relative viscosities of the mixtures first were calculated. The relative viscosity of a mixture is the ratio of the viscosity of the solution divided by the viscosity of the solvent, both measured at the same temperature and rate of shear. For the crossblended mixtures, it is assumed that the SEC Fraction-II component is the solvent, and so relative viscosities may be calculated by dividing each entry in Table 2 by the appropriate entry in Table 1. The viscosities of the SEC Fraction-II materials vary considerably and affect thc absolute viscosities of the mixtures. Specific viscosities then are calculated from relative viscosities by subtracting unity (one) from the relative viscosities. Reduced specific viscosities are calculated by dividing specific viscosities by the mass fraction of SEC Fraction-I, the solute, in a mixture. For example, the mass fraction of SEC Fraction-I in the eight mixtures listed in column 1 of Table 3 is 0.217.

Reduced specific viscosities are measures of compatibility of a system. Inspection of Table 3 reveals that the values range from 10, indicating a highly compatible system, to over 1,600, indicating a highly non-compatible system. Four of the sets of eight crossblends (columns 1, 2, 4, and 7 in Table 3) contain ~ 0.21 - 0.25 mass fraction of SEC Fraction-I, so that the concentrations of the dispersed components in these mixtures are more or less equivalent. The other three sets of crossblends (columns 3, 5, and 6 in Table 3) have lower concentrations of SEC Fraction-I (0.11 - 0.14). In most cases, the entries in columns 1, 2, 4, and 7 in Table 3 are much higher than the entries in columns 3, 5, and 6. The exceptions are the last entries in the columns, corresponding to mixtures in which the SEC Fraction-I component is derived from asphalt AAM-1. Therefore the concentration of SEC Fraction-I in a mixture usually strongly influences compatibility of the mixture. The AAM-1 SEC Fraction-I obviously is an unusual material. In columns 1, 2, 4, and 7, Table 3, even if the AAM-1 entries are discounted, reduced specific viscosity values vary greatly. Those mixtures in which SEC Fraction-I is derived from AAG-1 usually have relatively low reduced specific viscosities. Those mixtures in which the SEC Fraction-I is derived from AAD-1 have high reduced specific viscosities. The same trends are observed in the entries in columns 3, 5, and 6, Table 3. In the discussion on Black Plots above, it was emphasized that mixtures containing SEC Fraction-I components of AAD-1, AAG-1, and AAM-1 are unique, but in different ways. Reduced specific viscosities of mixtures containing SEC Fraction-I of the other five asphalts do not appear to vary as systematically. This indicates that specific interactions of these SEC Fraction-I materials with SEC Fraction-II materials influence compatibilities of mixtures. Inspection of columns 1, 2, 4, and 7 shows that the reduced specific viscosity values in column 1 tend to be somewhat higher than those in the other three columns. Therefore the SEC Fraction-II of AAA-1 is the least effective solvent of the four SEC Fraction-II materials. Similar considerations lead to the conclusion that SEC Fraction-II of AAF-1 is a better solvent than that of AAC-1. Concentrations of SEC Fraction-I in the two sets of crossblends are almost identical, and reduced specific viscosities in column 3 are much lower than those in column 5.

If the values in Table 3 are read across in rows instead of columns, it is evident that the nature of the SEC Fraction-II component of a particular mixture does not influence reduced specific viscosities as much as does the nature of the SEC Fraction-I component or the relative amounts of the two components. Nevertheless there is some influence of the SEC Fraction-II source. The data in Table 3 indicate that certain combinations of materials lead to unexpectedly large incompatibilities or the reverse.

CONCLUSIONS

Crossblended mixtures of asphalts have been prepared from two size exclusion chromatography fractions derived from eight different asphalts. The rheological properties of the mixtures were determined and it was found that, with one exception, the nature of the fraction assumed to correspond to the asphalt dispersed component and its relative abundance strongly influences rheological properties. These materials, which are the initial size exclusion chromatography eluates, are known to contain most of the polar, aromatic viscosity-building components of asphalts. The nature of the fraction corresponding to asphalt solvent components has a lesser influence on measured rheological properties of most crossblended mixtures, again with the exception of one set of mixtures.

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DISCLAIMER

ACKNOWLEDGMENTS

The authors thank the Federal Highway Administration for supporting this work under Contract No. DTFH61-92C-00170. Rheological measurements were performed by P. M. Harnsberger and F. A. Reid. J. Greaser prepared the manuscript. Figures were prepared by S. S. Kim.

Table 1. Yields of SEC Fractions of Eight SHRP Asphalts and Viscosities of SEC Fraction-II

Asphalt	Natural Abundance of SEC Fraction, Mass %		Viscosity (25°C; 1.0 rad/s) of SEC Fraction-II, Pa·s
	SEC Fraction-I	SEC Fraction-II	
AAA-1	21.7	78.3	506
AAB-1	20.8	79.2	1,367
AAC-1	13.6	86.4	8,602
AAD-1	21.2	78.8	336
AAF-1	13.3	86.7	53,350
AAG-1	11.2	88.8	62,380
AAK-1	24.8	75.2	1,124
AAM-1	31.8	68.2	26,350

Table 2. Viscosities (Pa·s) of Crossblended Mixtures of SEC Fractions of Asphalts, 25°C, 1.0 rad/s

Parent asphalt of SEC Fraction-I component of mixture	Parent asphalt of SEC Fraction-II component of mixture						
	AAA-1	AAB-1	AAC-1	AAD-1	AAF-1	AAG-1	AAK-1
AAA-1	65,200	179,600	230,100	36,100	642,400	204,400	155,100
AAB-1	90,500	148,400	220,800	36,800	384,900	403,600	198,600
AAC-1	95,900	148,000	156,100	43,300	571,900	362,950	251,300
AAD-1	177,300	223,100	225,400	59,200	884,300	764,800	240,700
AAF-1	101,400	185,400	225,900	50,000	507,000	466,300	217,400
AAG-1	36,700	97,300	138,600	26,600	502,400	405,500	164,750
AAK-1	95,800	145,100	185,700	31,300	344,600	332,250	165,450
AAM-1	3,500	10,200	26,500	3,000	114,900	125,900	10,600

Table 3. Reduced Specific Viscosity Values of Crossblended Mixtures of SEC Fractions of Asphalts, 25°C, 1.0 rad/s.

Parent asphalt of SEC Fraction-I component of mixture	Parent asphalt of SEC Fraction-II component of mixture						
	AAA-1	AAB-1	AAC-1	AAD-1	AAF-1	AAG-1	AAK-1
AAA-1	590	630	190	500	80	20	550
AAB-1	820	520	180	510	50	50	710
AAC-1	870	520	130	600	70	40	900
AAD-1	1,610	780	185	830	120	100	860
AAF-1	920	650	185	700	60	60	770
AAG-1	330	340	110	370	60	50	590
AAK-1	870	510	150	430	40	40	590
AAM-1	30	30	15	40	10	10	30

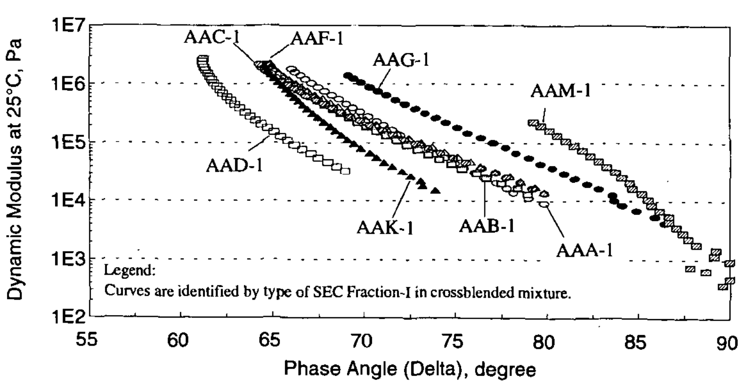

Figure 1. G* vs. phase angle for mixtures of SEC Fraction-II of AAA-1 (78.3%) with SEC Fraction-I (21.7%) of eight different asphalts.

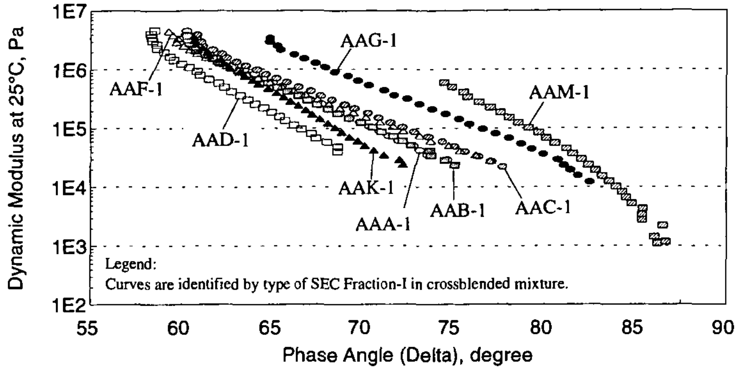

Figure 2. G* vs. phase angle for mixtures of SEC Fraction-II of AAB-1 (79.2%) with SEC Fraction-I (20.8%) of eight different asphalts.

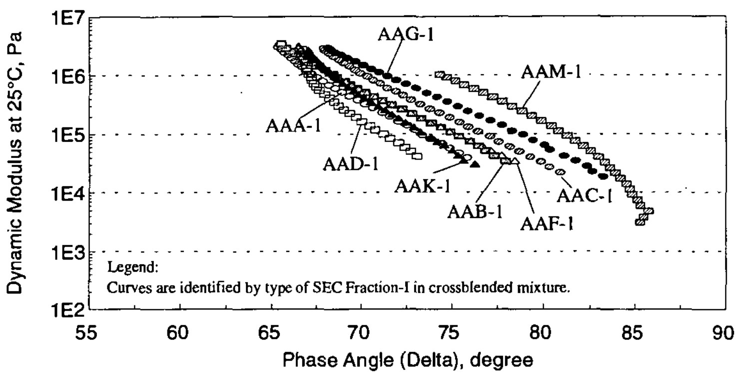

Figure 3. G* vs. phase angle at 25°C for mixtures of SEC Fraction-II of AAC-1 (86.4%) with SEC Fraction-I (13.6%) of eight different asphalts.

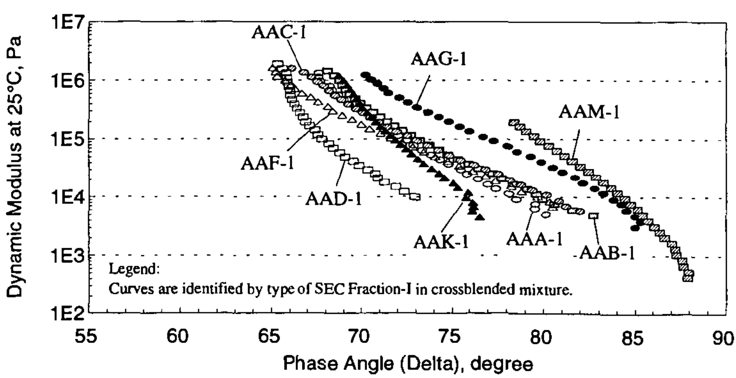

Figure 4. G* vs. phase angle for mixtures of SEC Fraction-II of AAD-1 (78.8%) with SEC Fraction-I (21.2%) of eight different asphalts.

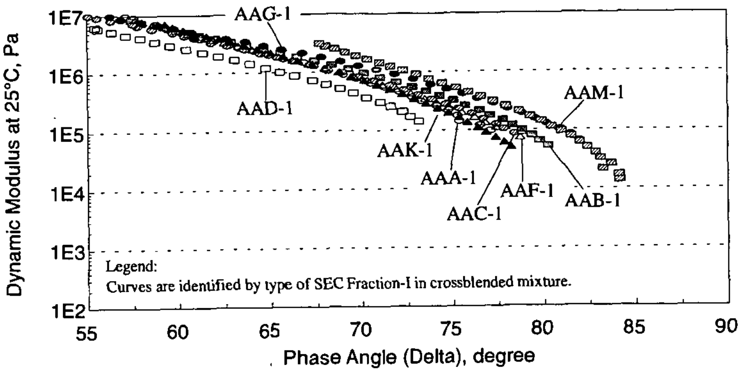

Figure 5. G* vs. phase angle for mixtures of SEC Fraction-II of AAF-1 (86.7%) with SEC Fraction-I (13.3%) of eight different asphalts.

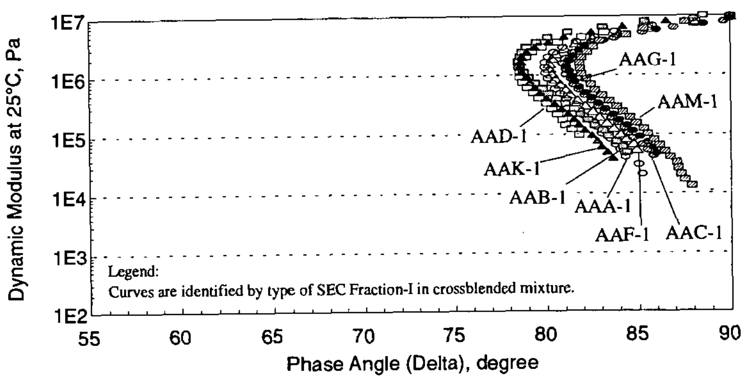

Figure 6. G* vs. phase angle for mixtures of SEC Fraction-II of AAG-1 (88.8%) with SEC Fraction-I (11.2%) of eight different asphalts.

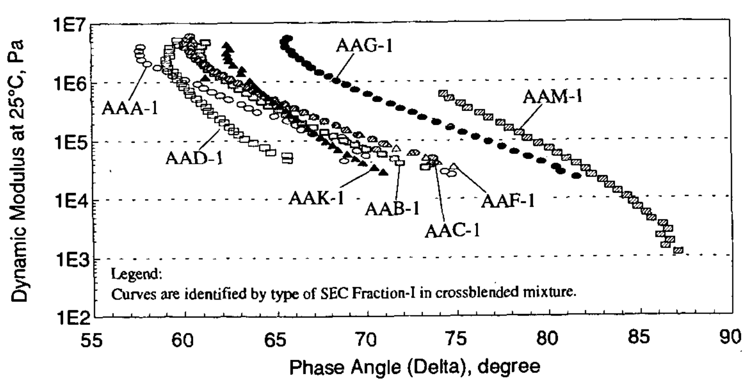

Figure 7. G* vs. phase angle for mixtures of SC Fraction-II of AAK-1 (75.2%) with SEC Fraction-I (24.8%) of eight different asphalts.